## Bidirectionality of the Electron Transfer in Photosystem I

The photosynthetic conversion of solar energy to chemical energy is the main mechanism of life support on Earth. Photosynthesis in higher plants and cyanobacteria occurs within two membrane pigment protein complexes, known as photosystem I (PSI) and photosystem II (PSII). Both of them catalyze efficient charge separation that takes place between redox cofactors, arranged into two highly symmetric branches A and B. Despite high symmetry, in PSII electron transfer proceeds only through A branch. Until recently, the general belief was that in PSI, electron transfer is also unidirectional, by analogy with PSII. However, while for PSII unidirectionality can be rationalized by the different functionalities of the two final quinone electron acceptors, this explanation does not hold for PSI. Here we report the direct observation by time-resolved high-field electron paramagnetic resonance spectroscopy of two structurally different charge-separated states corresponding to the A and B branches. Our data, in combination with kinetic studies done by others, prove the bidirectional nature of the electron transfer in PSI. Since evolutionary, PSI and PSII are believed to have a common ancestor, these results may shed light on how evolution tunes protein structure and energetics to control function.

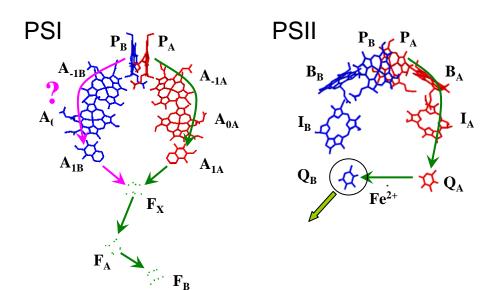


Figure demonstrates the analogy in the cofactor arrangement in PSI and PSII. In PSII the electron transfer occurs only along the A branch of cofactors (red). Argonne's magnetic resonance technique provides a unique way to directly detect the structure of transient charge separated states in both branches of protein, which allows us to confirm that in PSI, B branch (blue) is also active and, probably, is the main electron transfer pathway.